Methoden moderner Röntgenphysik I + II: Struktur und Dynamik kondensierter Materie

Vorlesung zum Haupt/Masterstudiengang Physik
SS 2009

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Trends in Spectroscopy

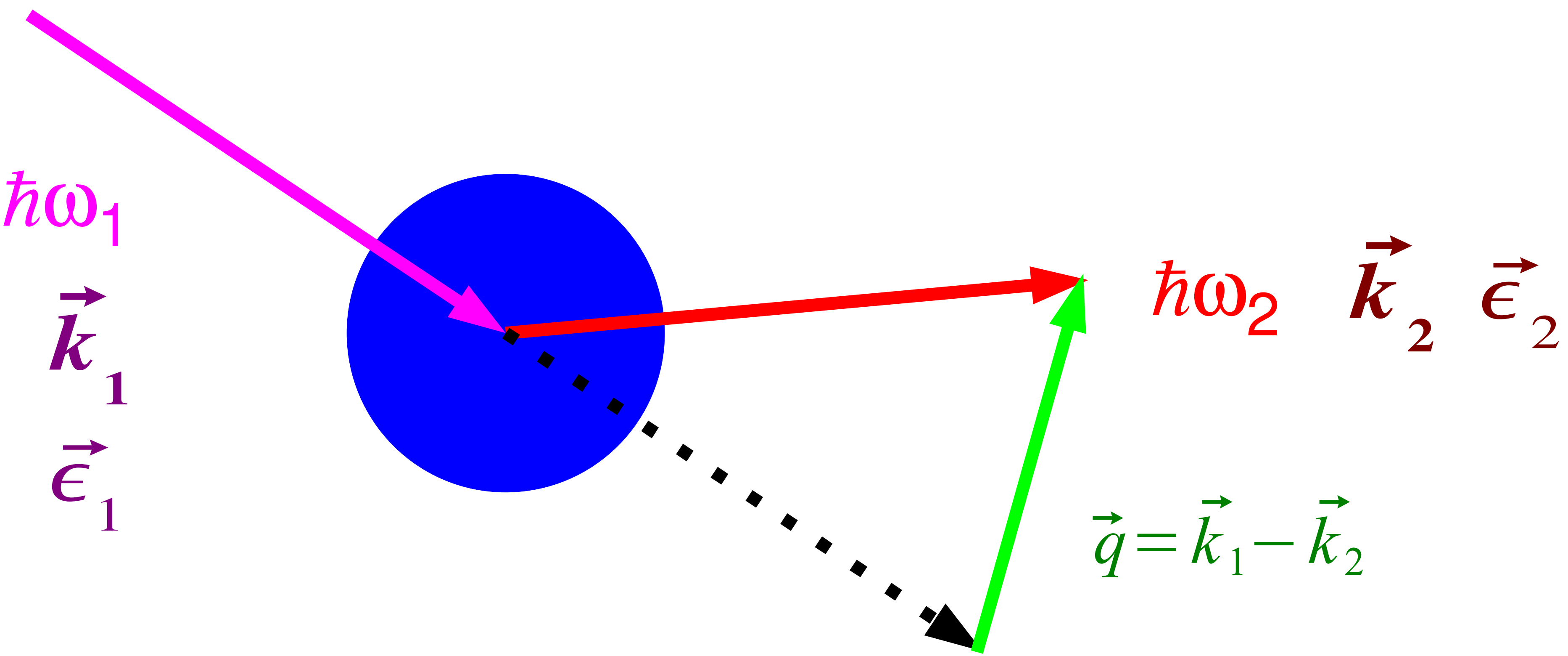
23.4.	Wolfgang Caliebe	IXS
28.4.	Wolfgang Caliebe	IXS
30.4.	Ralf Röhlsberger	NRS
5.4.	Wolfgang Drube	XPES

Inelastic X-Ray Scattering

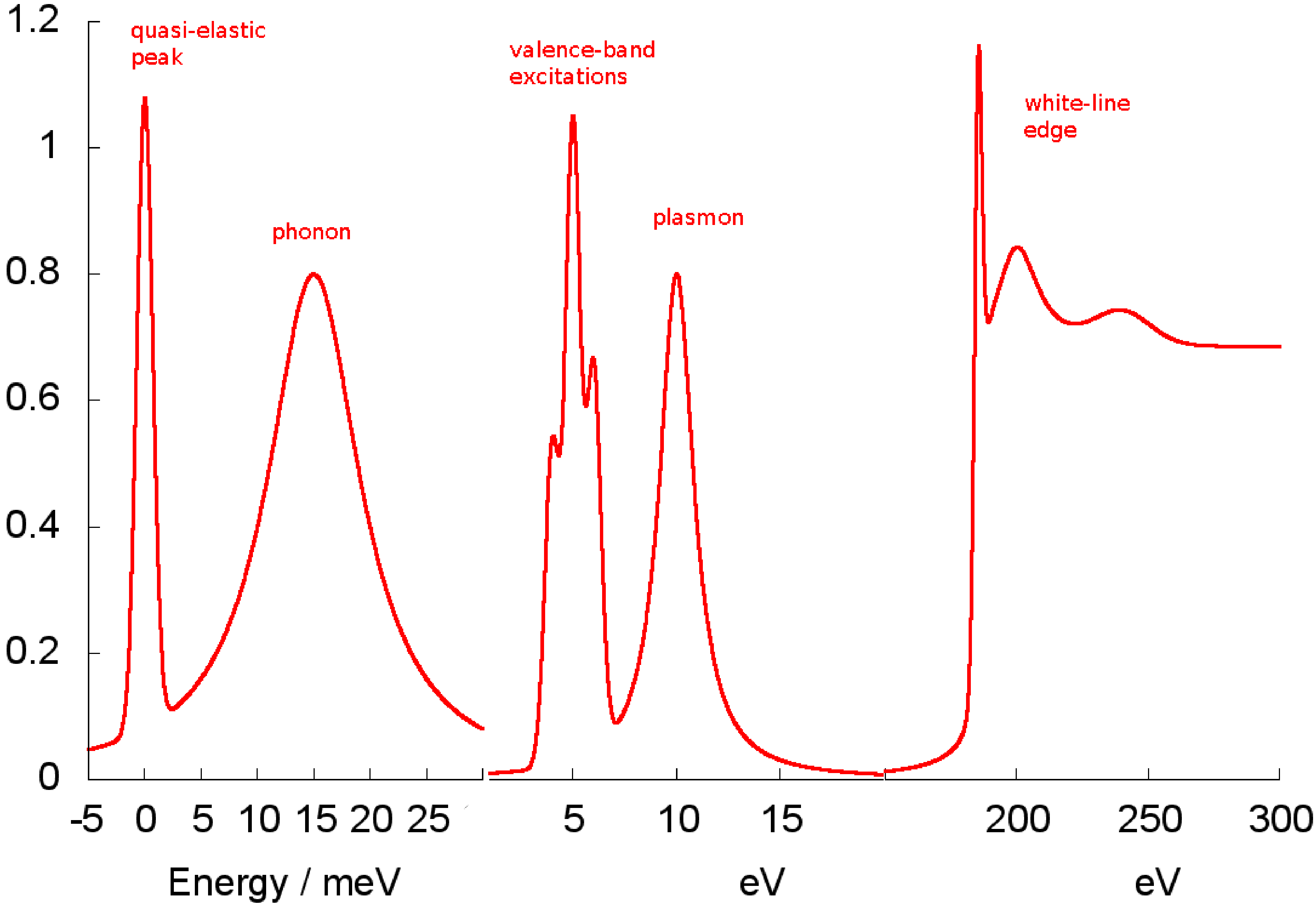
Measure energy loss (or gain) of scattered photon

- High energy resolution
- Good momentum resolution

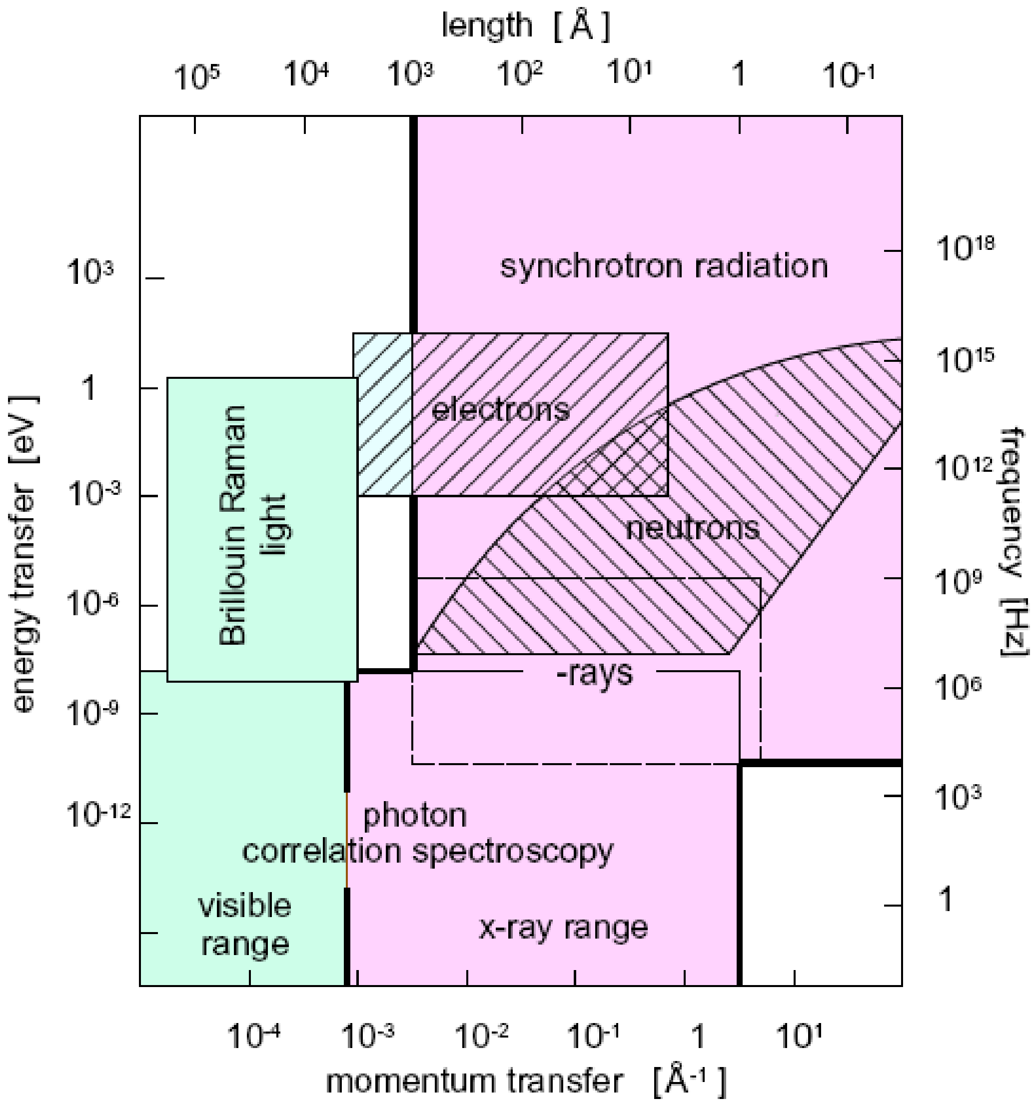
$S(\mathbf{q},\omega)$



Different types of excitations in solids



Different Probes to study excitations in solids



E. Burkel, Rep. Prog. Phys. **63** 171 (2000)

Differences in experiments based on resolution and incident energy:

non-resonant:

- meV: Phonons
- eV: Plasmons, band excitations, soft absorption edges, Compton scattering

resonant (incident energy tuned to an absorption edge):

- Resonant inelastic scattering
- Resonant emission spectroscopy

Literature?

Differences in experiments based on resolution and incident energy:

non-resonant:

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Ashcroft/Mermin Solid State Physics (1976):
"In general the resolution of such minute photon frequency shifts is so difficult that one can only measure the *total* scattered radiation of all frequencies, as a function of scattering angle, in the diffuse background of radiation found at angles away from those satisfying Bragg condition."

Literature

Textbooks on Solid State Physics:
- Charles Kittel, Introduction to Solid State Physics
- Ashcroft, Mermin, Solid State Physics
- K. Kopitzki, Einführung in die Festkörperphysik

Phonons
- Stephen Lovesy, Theory of Neutron Scattering from Condensed Matter

Summer Schools
- Jülich Spring School
- Grenoble HERCULES Course

Scientifc Journals
- Review articles by Sette et al., and Burkel et al.

Today: Phonons (Lattice Excitations), Fast Sound in Water

Double differential scattering cross section ↔ $S(\mathbf{q},\omega)$

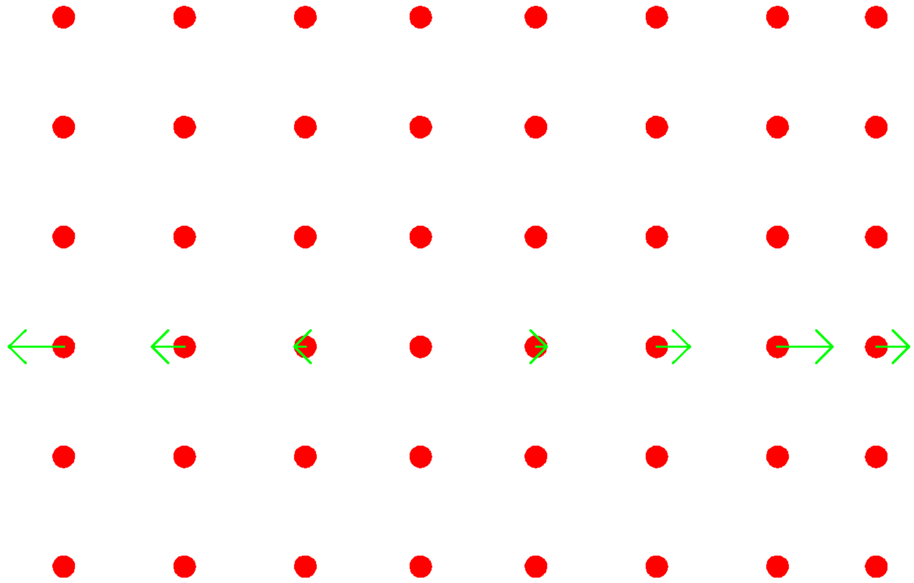
Phonons

instrumentation for IXS with meV resolution

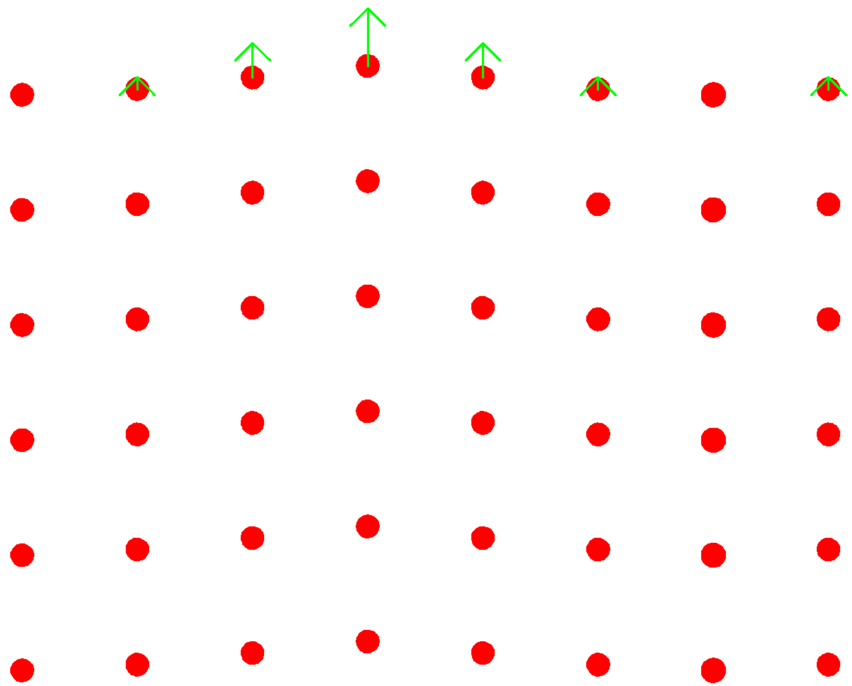
Examples

- phonons in Pu
- phonons in Rb at high pressure
- fast sound in water

Lattice Excitations - Phonons



Longitudinal wave: Lattice planes change distances



Transversal wave: Lattice planes change angles

Dispersion of a Phonon (classical approach)

Assume that the force between two planes with distance p is

$$C_p \cdot (u_{s+p} - u_s)$$

C_p: Force constant

Total force on plane s: $F_s = \sum_p C_p \cdot (u_{s+p} - u_s)$

Equation of motion for plane s $M \frac{d^2 u_s}{dt^2} = \sum_p C_p \cdot (u_{s+p} - u_s)$

Look for solutions with time-dependence $\exp(-i\omega t)$

$$-M\omega^2 u_s = \sum_p C_p \cdot (u_{s+p} - u_s)$$

Solution: $u_{s+p} = u \exp(i(s+p)ka)$

k: wave vector
a: lattice constant

Use solution for previous equation:

$$-M\omega^2 u \exp(iska) = \sum_p C_p \cdot (u \exp(i(s+p)ka) - u \exp(iska))$$

Divide by u exp(iska):

$$M\omega^2 = -\sum_p C_p \cdot (\exp(ipka) - 1)$$

Translational invariance: $C_p = C_{-p}$

$$M\omega^2 = -\sum_{p>0} C_p \cdot (\exp(ipka) + \exp(-ipka) - 2)$$

Finally, get:

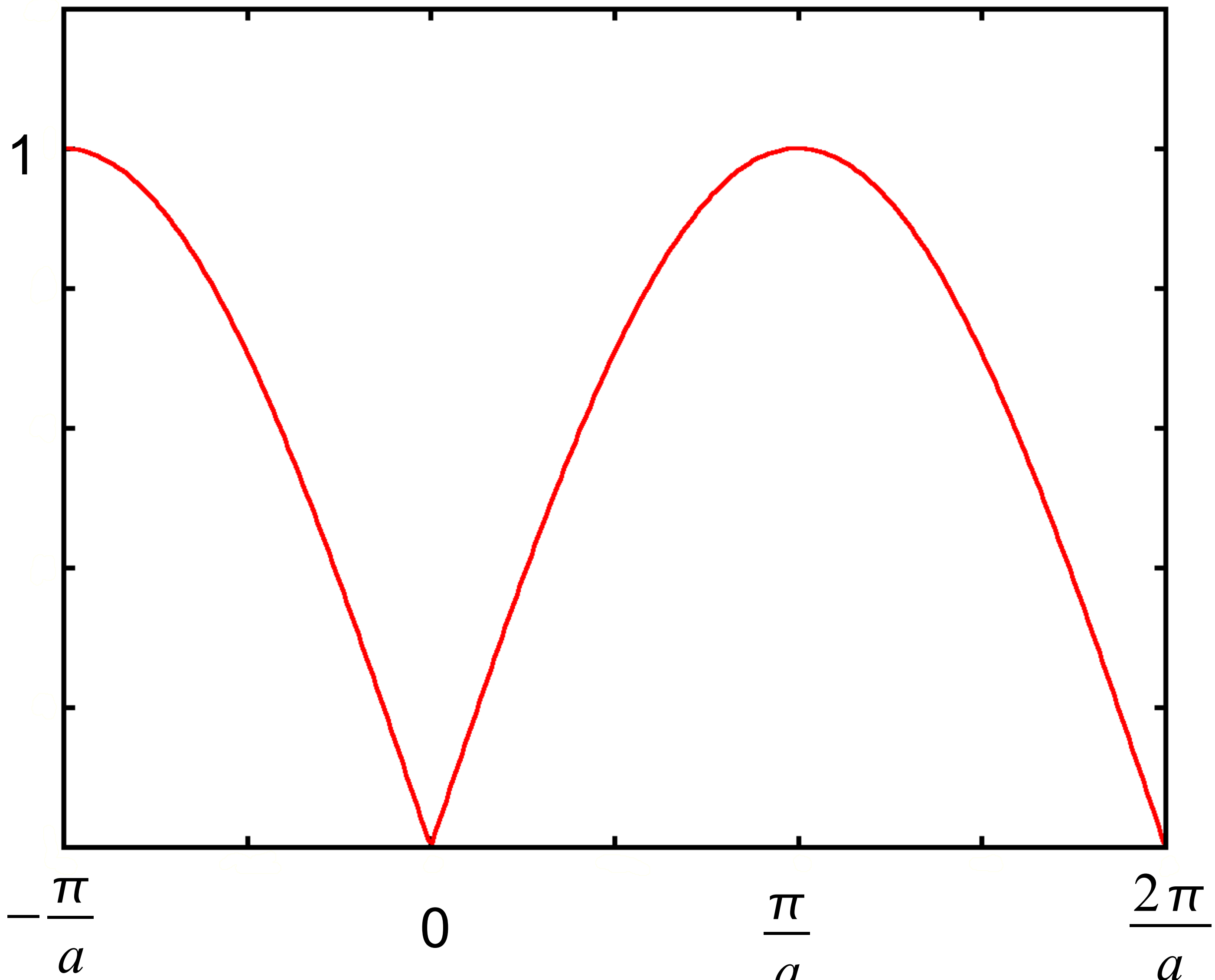
$$M\omega^2 = \frac{2}{M} \sum_{p>0} C_p \cdot (1 - \cos(pka))$$

Dispersion relation

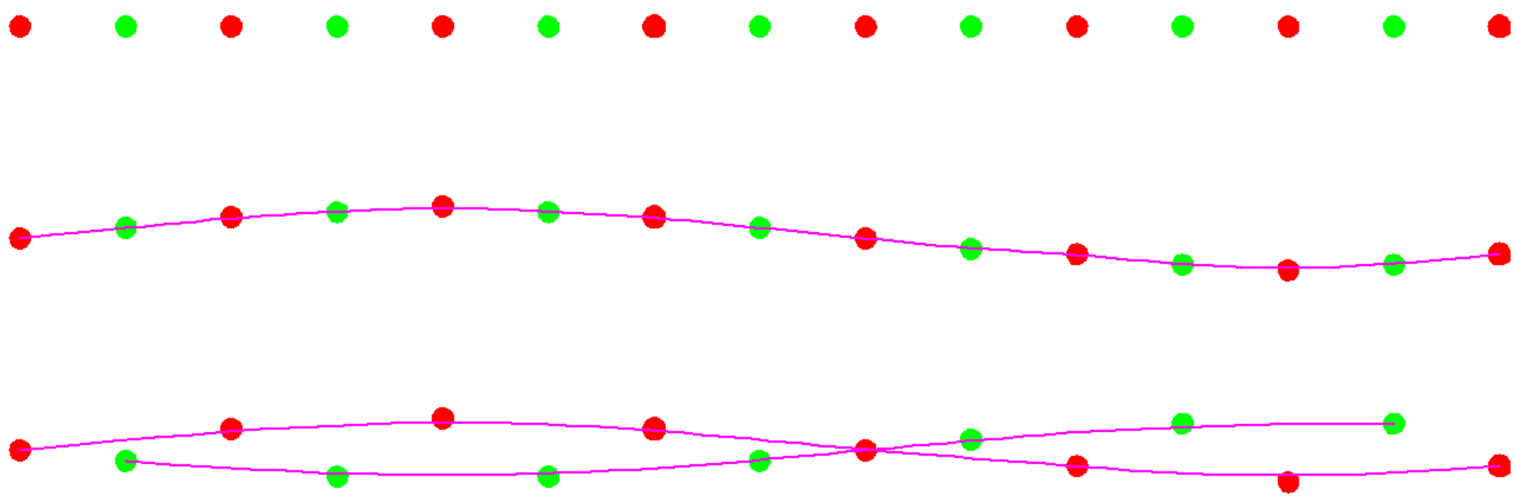
relates ω and k

Exchange interaction only between neighboring planes:

$$\omega^2 = (4C_1/M)\sin^2\left(\frac{1}{2}ka\right)$$



Dia-atomic basis



Equilibrium positions

Acoustical mode

Optical mode

Transversal waves

Exists also for longitudinal waves

Dispersion of Phonons

Same idea: Start with force on planes
now 2 different masses
just forces between neighboring planes

$$M_1 \frac{d^2 u_s}{dt^2} = C_p \cdot (v_s + v_{s+1} - 2 u_s)$$

$$M_2 \frac{d^2 v_s}{dt^2} = C_p \cdot (u_s + u_{s+1} - 2 v_s)$$

Same formalism and tricks as before:

$$M_1 M_2 \omega^4 - 2\mathrm{C}(M_1 + M_2)\omega^2 + 2\mathrm{C}^2(1 - \cos(ka)) = 0$$

Search for solutions at $k \approx 0$

$$\omega^2 \approx 2C\left(\frac{1}{M_1}+\frac{1}{M_2}\right)$$

Optical branch

$$\omega^2 \approx \frac{2C}{M_1+M_2} k^2 \frac{a^2}{4}$$

Acoustical branch

and $k = \pm\pi/2a$

$$\omega^2 = 2C/M_1 \quad ; \omega^2 = 2C/M_2$$

Can we apply the same formalism as last week?

Photons interact with the electrons
Photons interact significantly weaker with the nucleus

Why can we try to observe anything:

Adiabatic Approximation:
Electrons adapt to 'slow' motions of nucleus

Separate wave-function |S> into product of wave-functions of electron $|S_e>$ and nucleus $|S_n>$:

$$|S> = |S_e>|S_n>$$

Electrons are not excited

$$|I>=|I_e>|I_n> \qquad |F>=|I_e>|F_n>$$

F. Sette & M. Krisch, Inelastic X-Ray Scattering from Collective Atom Dynamics, *in* Neutron and X-Ray Spectroscopy, ed. F. Hippert et al., Spinger (2006)

Hamilton-operator for scattering

Hamilton-operators:

$$H^{(1)}_{int} = \sum_j \frac{e^2}{2mc^2} \vec{A}_j^2$$ Radiation field

|I> and |F> are eigenstates of H_0 with eigenenergies E_I and E_F, and |I> and |F> are orthogonal: <F|I>=0

Ignore all terms in second order in A

$$\hbar\omega = \hbar\omega_1 - \hbar\omega_2$$

$$\frac{d^2\sigma}{d\Omega\, d\omega_2} = r_0^2 \frac{\omega_2}{\omega_1} (\vec{\epsilon}_1 \cdot \vec{\epsilon}_2)^2 \sum_{I,F} \left| \langle F | \sum_j \exp(i\vec{q}\cdot\vec{r}_j) | I \rangle \right|^2 \delta(E_F - E_I - \hbar\omega)$$

Polarization factor

Conservation of energy

Dynamic structure factor

$$S(\vec{q},\omega)=\sum_{I,F}\left|\langle F|\sum_j \exp(i\vec{q}\cdot\vec{r}_j)|I\rangle\right|^2 \delta(E_F-E_I-\hbar\omega)$$

$$S(\vec{q},\omega)=\frac{1}{2\pi\hbar}\int_{-\infty}^{+\infty} dt\,\exp(-i\omega t)\int d\vec{r}\,\exp(i\vec{q}\cdot\vec{r})G(\vec{r},t)¿$$

*G(**r**,t)*: pair correlation function

$$G(\vec{r},t)=\frac{1}{N}\int d\vec{r}\,'\langle\hat{\rho}(\vec{r}\,'-\vec{r})\hat{\rho}(\vec{r}\,',t)\rangle$$

Important property:

$$\langle\hat{\rho}(\vec{k},t)\hat{\rho}^{+}(\vec{k},0)\rangle=\langle\hat{\rho}^{+}\hat{\rho}(\vec{k},t+i\hbar\beta)\rangle$$

$$\beta=1/k_B T$$

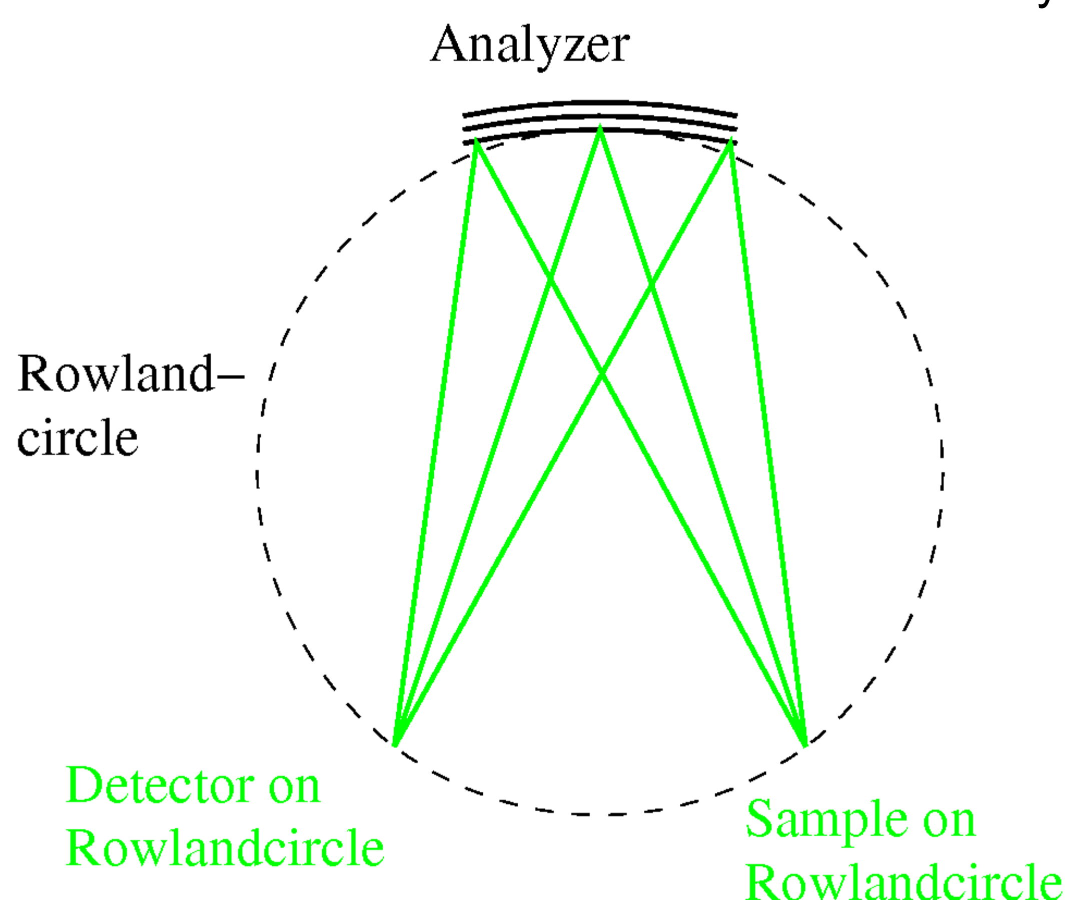
Condition of detailed balance:

$$S(\vec{q},\omega)=\exp(\beta\hbar\omega)S(-\vec{q},-\omega)$$

Crystal Spectrometer

Best way to obtain high energy resolution!
Thousands of small, flat crystals on a spherical surface
close to backscattering geometry
source and crystal sizes contribute to resolution
large solid angle

Johann Geometry



Typical dimensions:

Analyzer diameter	100mm
Rowland circle	6000mm

Why Backscattering-Geometry?

How to calculate the energy resolution? Ahlefeld, 60ies

Braggs Law: $2d\sin\Theta = \lambda$

partial derivatives give: $\Delta E/E = \Delta\Theta \cdot \cot\Theta + \Delta d/d$

cotanΘ=0 for 90^0

$$\Delta\tau = \frac{16\pi r_0}{V\tau}|F(q)| \qquad \left(\tau = \frac{2\pi}{d}\right)$$

Silicon, Germanium:

$$\frac{\Delta\tau}{\tau} = \frac{4r_0}{\pi a} \cdot \frac{1}{h^2+k^2+l^2} \cdot f(q) \cdot \left\{ \begin{array}{c} 8 \; for \; h+k+l=4n \\ 4\sqrt{2} \; for \; h,k,l \; all \; odd \end{array} \right\}$$

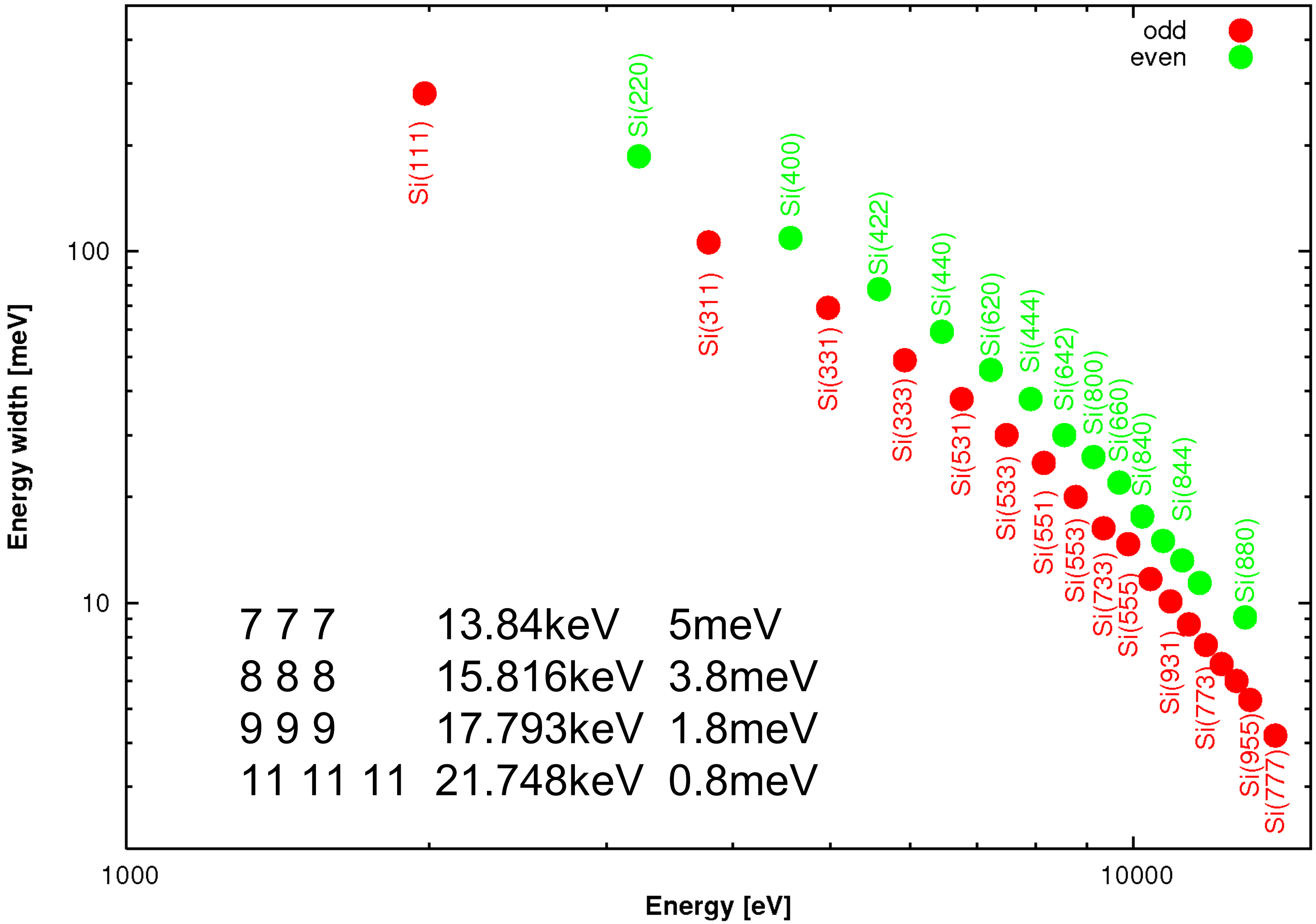
Energy-momentum relation different for

photons and neutrons:

$E_x \sim k$ $E_n \sim k^2$

$\Delta E_x \sim 1/\sqrt{(E_x)} \cdot f(q)$ $\Delta E_n \sim f(q)$

Energy Resolution of different Si-reflections at backscattering



What about the monochromator?

Specifications: good energy resolution (similar to analyzer)
energy close to backscattering energy of analyzer
low tunability (few tens of meV)
high throughput

Now, we use a backscattering monochromator!

And we have to use different tricks for energy scans!

We cannot tune the angle for an energy scan

- Change in energy resolution
- Beam-motion for single backscattering monochromator
- Large motions for double-crystal fixed-exit monochromator

We have to change the lattice constant instead

$$\frac{\Delta E}{E} = \frac{\Delta d}{d} = \alpha T$$

$\alpha = 2.58 \cdot 10^{-6}\ K^{-1}$

Example: E=18keV, ΔE=1meV $\Rightarrow$ T=0.02K

Technical Challenge

Keep the energy of the analyzers stable at room temperature

1mK stability over few hours

heat and cool the monochromator for energy scans

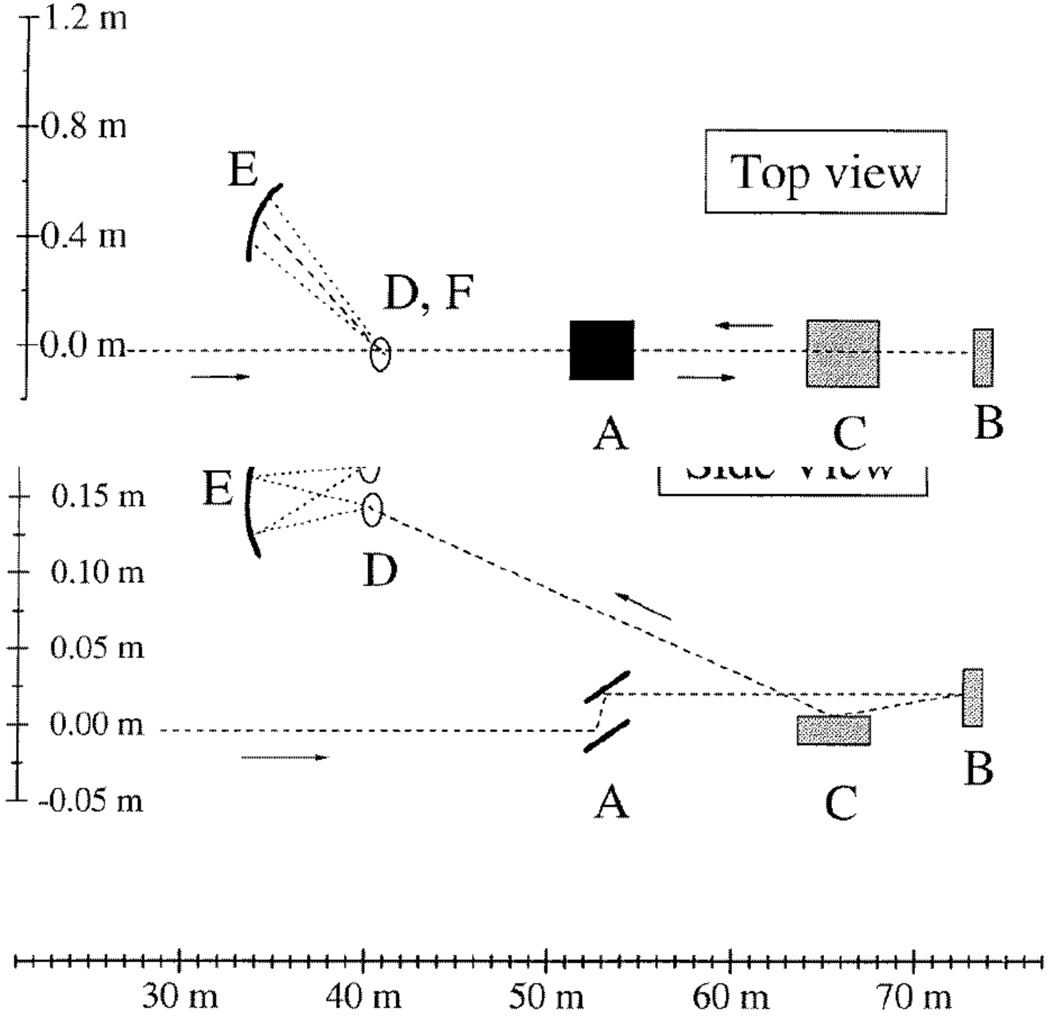
measure both temperatures with a precision of 0.5mK

Very important:

need pre-monochromator for the white beam from the undulator

power in (pre-)monochromatic beam can heat the high resolution monochromator

Experimental Set-up



F. Sette, G. Ruocco, J Phys. Condens. Matt.**11** R259-R293 (1999)

Scientific Results

Phonon in Pu
Phonon is Rb under high pressure
Fast Sound in water

Phonons in Plutonium

Plutonium 5f-electron system, strange properties

- 6 different phases between room temperature and melting
- Large volume changes
- Density of liquid higher that that of solid

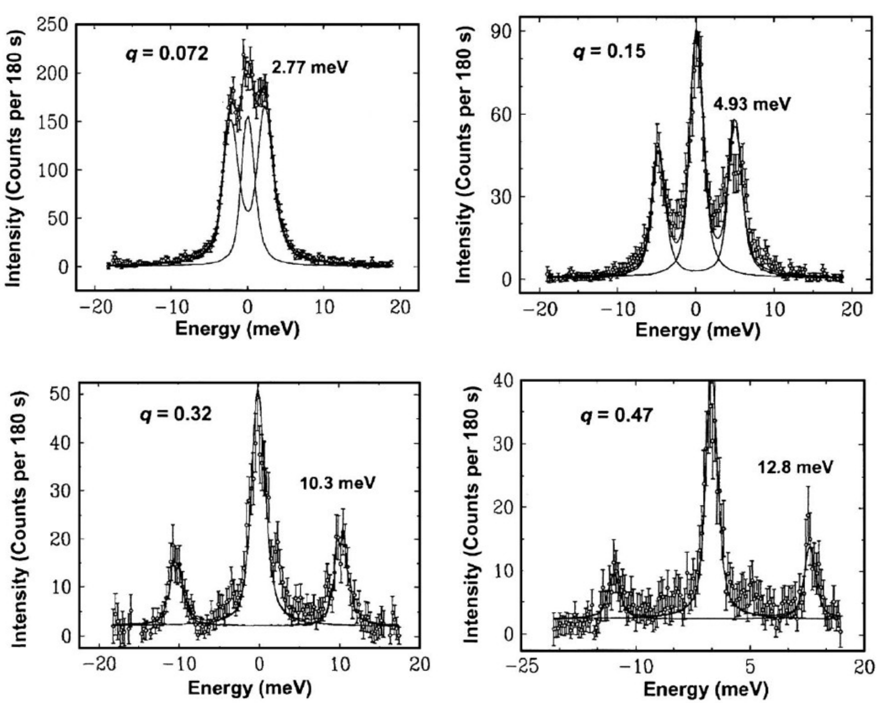
Neutrons have disadvantages

- Large thermal absorption cross section for Pu
- No single crystals with mm-dimensions

X-Rays can be applied to this problem

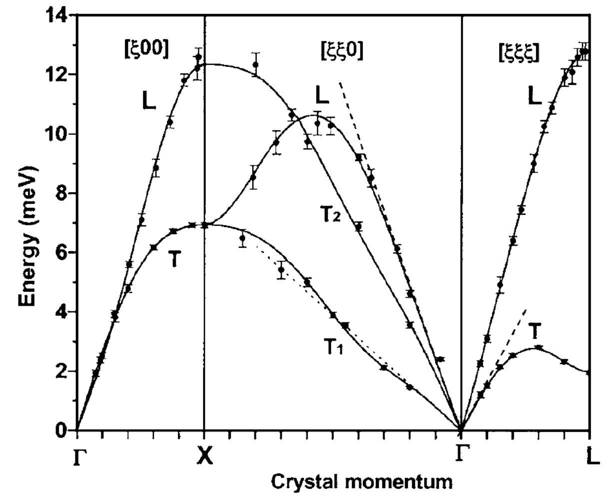
+ High absorption, but also high cross section
+ Micron-sized beam fits micron-sized single crystals

Experimental Results

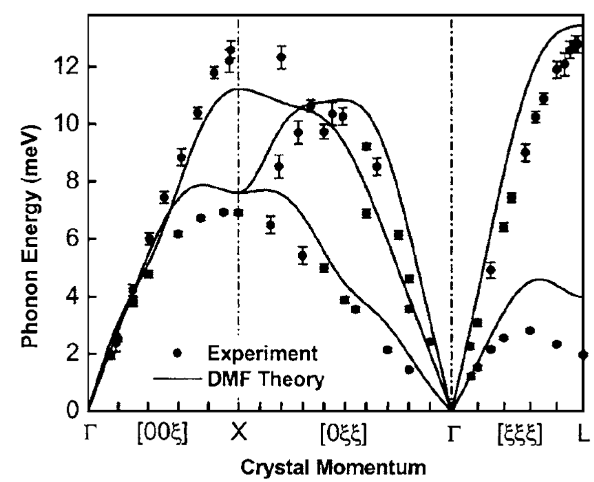


IXS data of Pu at different momentum transfers

J. Wong, M. Krisch et al., Phys. Rev. B, **72** 06415 (2005), Science **301** 1078-1080 (2003)



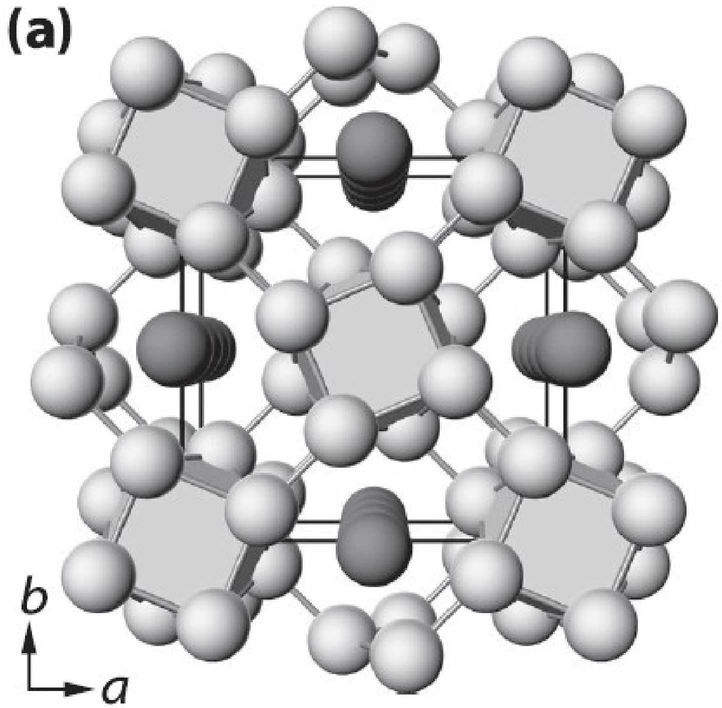
Born-van Karman fit to experimental dispersion



MD-simulations

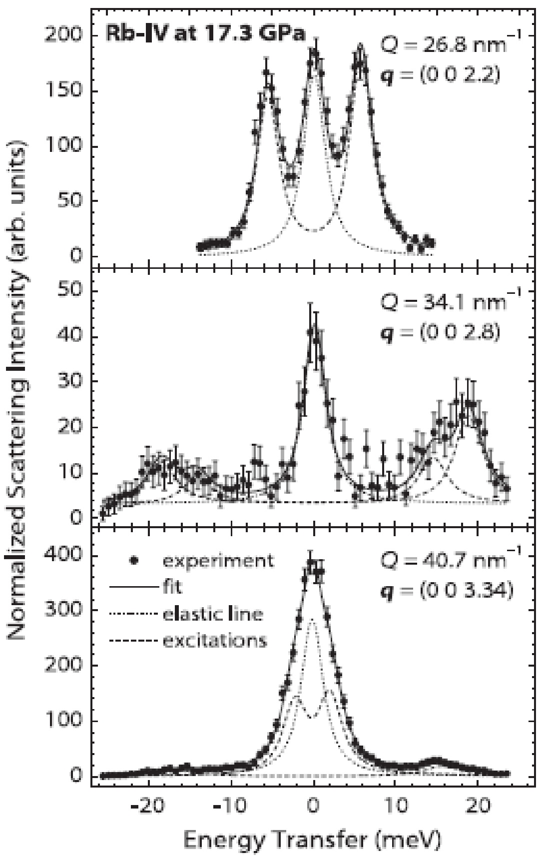
Phonons in Rubidium at High Pressure

Alkali-metals 'simple' systems with bcc-structure
exhibit interesting structures under high pressure
structures become more complex with lower symmetry

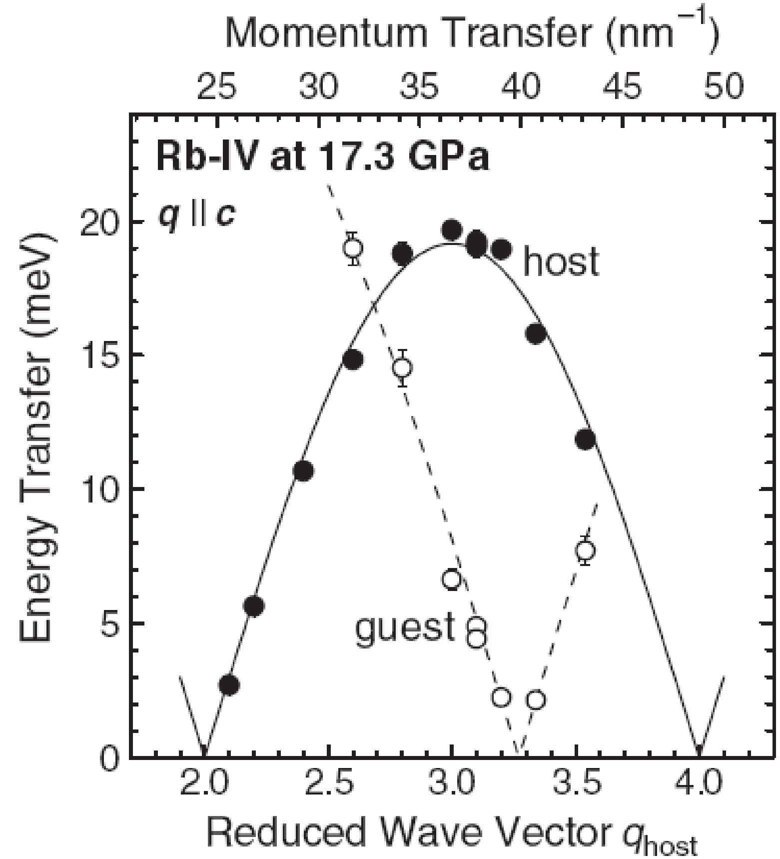


Incommensurate structures with framework of host atoms and 1D-channels of guest atoms

Experimental Results



IXS-spectra of Rb at high pressure at different momentum transfer



Dispersion of the phonon in the direction of the channels, host and guest have different dispersions

I. Loa et al., Phsy. Rev. Lett. **99** 035501 (2007)

Fast Sound in Water

Molecular Dynamics calculations for S($\mathbf{q}$,ω) of water (1974):

two distinct features in S($\mathbf{q}$,ω) between 3 and 6nm^{-1}

two propagation modes with sound velocities 1500 and 3000m/s

first one already observed with ultrasound and Brillouin-scattering experiments

new, unknown sound velocity called 'Fast Sound'

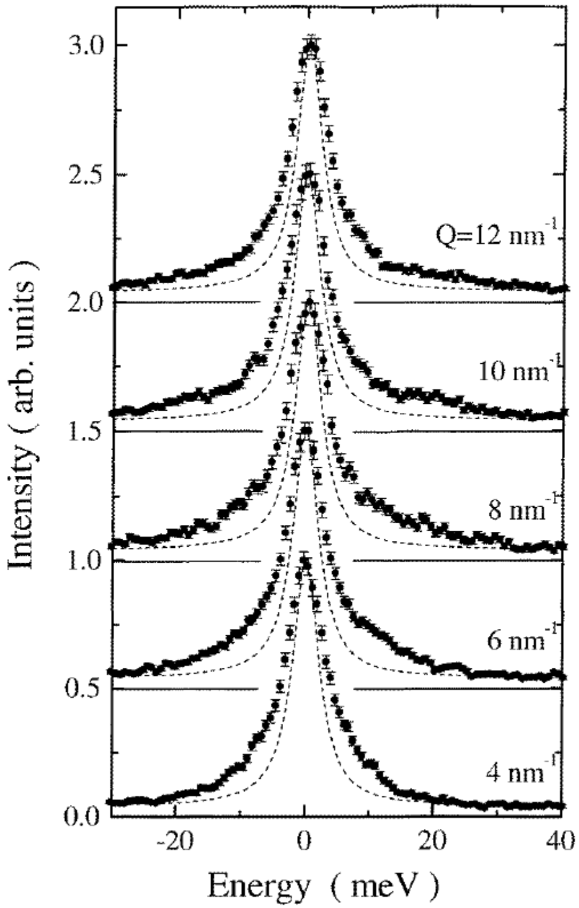
associated with hydrogen-bond network

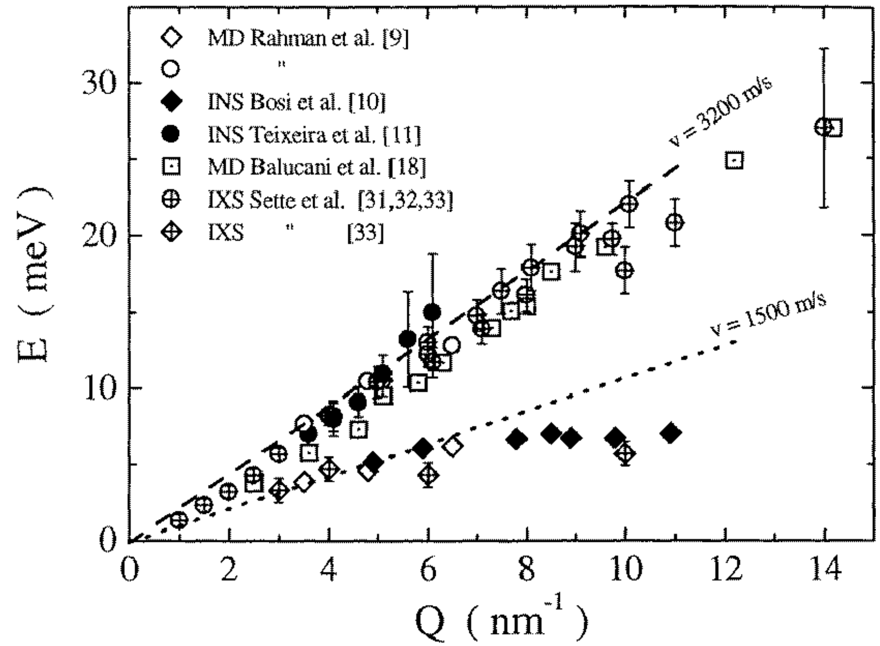
first neutron experiments observed only the 1^{st} excitation (1978)

later neutron experiments observed only the 2^{nd} excitation

IXS-experiments can see both (1995)

Experimental Results

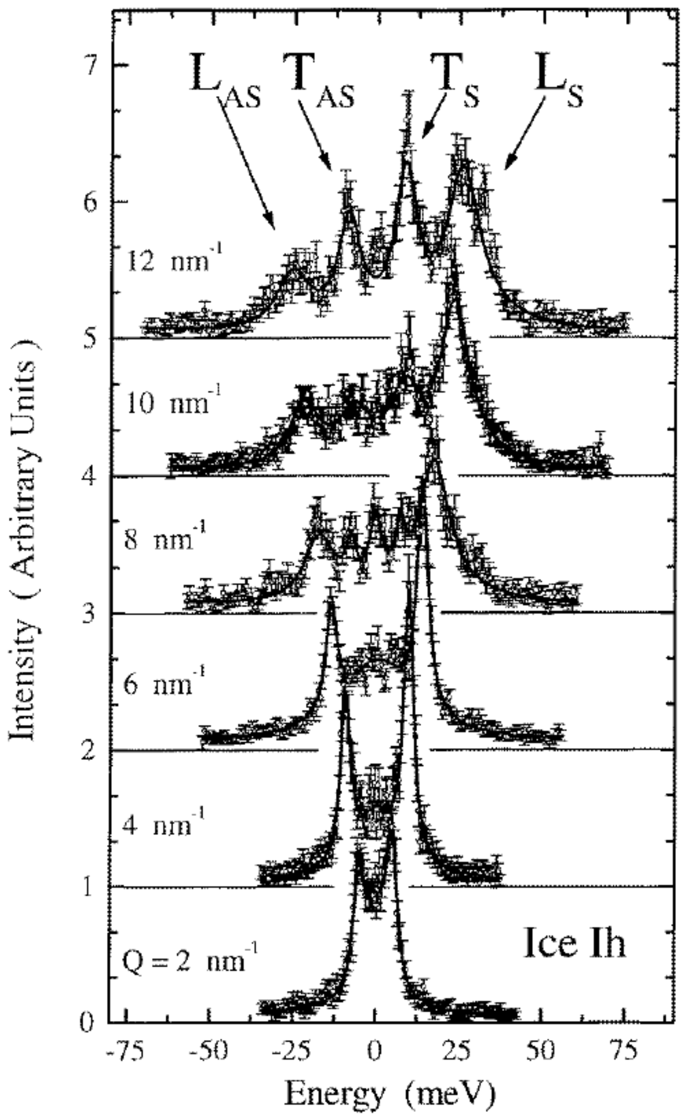




Dispersion of the two phonons measured with different probes, the two different speeds of sound are clearly observable

IXS-spectra of water at 5°C for different momentum transfer

G. Ruocco, F. Sette, J. Phys: Condens. Matt. **11** R259-R293 (1999)



IXS-spectra of Ice_h at different momentum transfers